

TPO-Clay 나노복합재료의 동적·점탄성적 거동

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Rheological and Dynamic Behavior of TPO-Clay Nanocomposite

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Introduction

Polypropylene(PP) is a versatile thermoplastic material processable with many conventional processing techniques and used in many different commercial applications. And EPDM rubbers are well known for high toughness and environmental stability. Blends with a high content of PP are utilized as a high-impact PP, where as blends with a high content of EPDM can be used as thermoplastic elastomers[1]~[4]. Therefore TPOs(Thermoplastic polyolefin elastomer) based on PP and EPDM has good weather resistance, heat resistance, and their cost is lower than other product which have similar properties, and they are used for automotive, electronic, construction, and living products. It is an important objective in TPO development to improve the thermal and mechanical property by means of EPDM and clay hybrids. Such composites exhibit the drastic improvement in mechanical and thermal properties. Organically modified clay mineral with different organic modifier and PP/EPDM were melt blended in a twin screw extruder and structure-property relationship of the resulting blends were investigated. The effects of the clay mineral dispersity on the PP/EPDM were discussed. Enhanced mechanical properties were interpreted in terms of the formation of dispersed nanoparticles consisting of the intercalated layered silicate. Basic correlations between polymer morphology, silicate superstructures, glass transition temperature, stiffness and toughness of nanocomposites were investigated as a function of layered silicate content. From X-ray diffraction measurement of the blends, a remarkable geometrical structure of the clay mineral in the blend was expected. The effects of the clay content on dynamic behavior were also studied with DMTA and rheological property measurements were performed on ARES(Rheometrics Scientific) using frequency sweep with cone and plate geometry.

Experimental

Commercial grades of isotactic PP(Korean Petrochemical Ind. Co) with weight average molecular weight, $M_w=380,000$, number average molecular weight, $M_n=54,000$), an EPDM (KEP240, ethylene content=56wt%) were used for blending. Maleic anhydride grafted EPDM(Royaltuf) was used as a functionalized compatibilizer. We investigated dynamic mechanical and rheological behavior of composites by using the different types of organoclay : C25, C30 modified alkyl type and hydroxyl type ammonium ion respectively. The gallery of organoclay was increased by using a functionalized compatibilizer, and was

induced fully exfoliated state. The simple blends of PP/EPDM and clay composite with different dispersion state have been prepared using a twin screw extruder at 200°C. A peroxide was used in combination with trimethylolpropanetriacrylate(TMPTA) as a multifunctional monomer.

Results and discussion

Characterization and dispersion state of TPO/clay nanocomposite were listed in table 1. They were not fully exfoliated, but intercalation state was obtained regardless of clay type. Long chain polymer can be intercalated better in the gallery of layered silicate modified with alkyl type ammonium ion than hydroxyl type one. Because the interaction between polymer and organoclay modified with alkyl type ammonium ion is stronger, therefore polymer chain could be better intercalated in C25 than in C30 which was modified with hydroxyl type ammonium ion. Even if certain mechanical properties such as modulus and tensile strength of PP is decreased by blending with rubbery materials, small amount loading of C25 composite resulted in increased moduli in Figure 1[5]. At high content, however, drastically increased modulus was not seen. This implied that there were three dispersion states; exfoliation, intercalation, and immiscible state simultaneously.

Figures 2, 3 and Figure 4 show rheological properties measured at 200°C. The storage moduli for all composites exhibit increase with the clay content at given frequency range. Rheological properties were determined to examine the presence of particle network formation via interparticle interaction and self-assembly[6]. We observed the effect of clay content and type for TPO/clay composite. The curves for A and B-series were slightly shifted to higher moduli, as expected for the filler effect. The typical slopes of G' and G'' for monodispersed polymer are 2 and 1, respectively. The properties of MP0 showed the normal material response of a narrow distributed thermoplastic polymer, and as increasing clay content, strongly increased value of storage modulus was found and the slope of the curve approach zero at low frequency[4]. Such behavior is an indication of network formation involving assembly of individual platelets being composed of silicate layers[6].

The complex viscosities of all composites increase monotonically than simple blend of PP and EPDM. At the high content, the curves of composites showed the viscosity yield, because attractive forces between immiscible clay minerals were such that they formed a three-dimensional network[7].

Conclusion

In conclusion, the particles of layered silicates were dispersed at the nanometer level, and the dynamic and viscoelastic behavior of TPO-clay composite were influenced by the clay type and dispersion state.

Reference

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Table 1. Characterizations and mechanical properties of nanocomposites

Code	d-spacing (Å)	Elongation (%)	Yield strength (MPa)	Fracture strength (MPa)	Young modulus (MPa)
MP0 ^a	18.82	813	19.59	16.76	3376
A2 ^b	36.53	650	21.39	17.22	2438
A5	36.92	455	23.97	19.20	2853
A10	36.83	222	24.52	21.79	5158
B2 ^c	33.68	567	20.58	18.16	4954
B5	33.94	485	21.38	18.04	5016
B10	33.85	352	23.16	21.37	4948

a MP0 : PP/EPDM/MA-g-EPDM=60/30/10 (TPO)

b A-series : TPO/C25

c B-series : TPO/C30

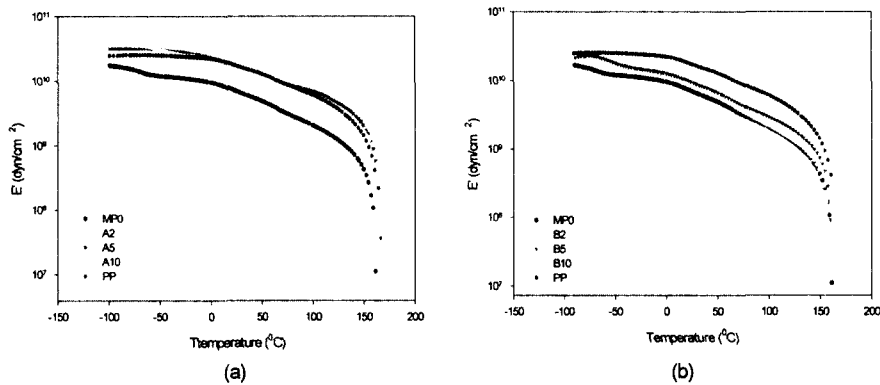


Figure 1 Dynamic mechanical properties of TPO-clay nanocomposite : (a) TPO-C25, (b) TPO-C30.

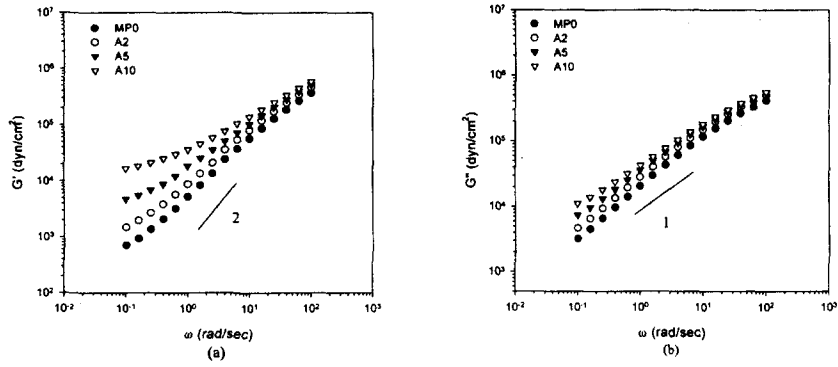


Figure 2 Dynamic complex moduli for TPO-C25 nanocomposites at 200 °C :
 (a) Storage modulus, (b) Loss modulus.

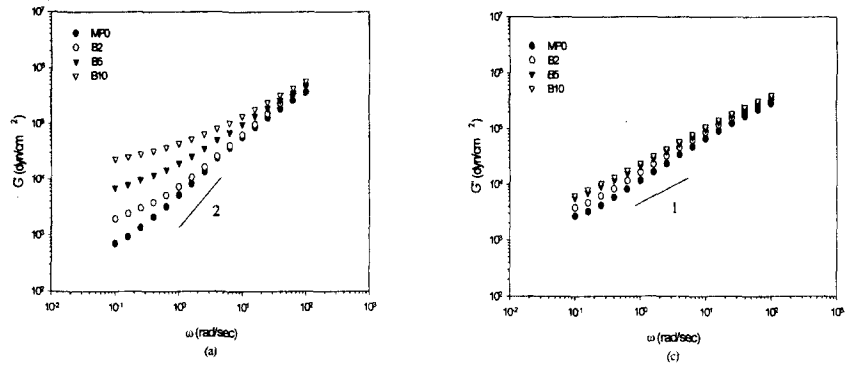


Figure 3 Dynamic complex moduli for TPO-C30 nanocomposites at 200 °C :
 (a) Storage modulus, (b) Loss modulus.

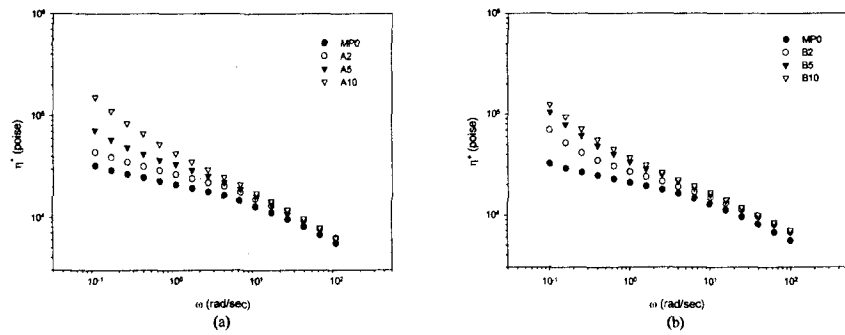


Figure 4 Complex viscosity vs frequency of TPO/clay nanocomposite :
 (a)TPO/C25, (b)TPO/C30.